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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se référer à la description.)

Dental composition comprising ethylene imine compounds an non-reactive  
accelerators

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58741EP002  
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## **Dental Composition Comprising Ethylene Imine Compounds and Non-Reactive Accelerators**

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The present invention relates to a composition with enhanced speed of set, especially to a method of making rubber-like elastomers with improved hardening characteristics.

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Compared to known ethylene imine group containing polyether materials, herein called slow-setting materials, the materials according to the invention have a shorter time of set. These formulations are called fast-setting materials.

15

Usually the speed of set of dental formulations is adjusted by varying the amount of reactive components, e.g. varying the amount of the polymerizable compound(s) and varying the amount the initiator(s) accordingly and/or varying the amount of the retarder(s).

Aziridines which are also known as ethylene imine compounds can be converted into highly molecular polyamine compounds by means of catalysts which introduce and thus initiate polymerization.

20

In this respect US 3,453,242 describes curable elastomers from polyethers and ethylene imine derivatives. The polymers are substantially linear in structure and contain ethylene imine groups especially at the ends of the chain to obtain rubber-like products.

DE 100 58 846 A1, DE 197 53 456 A1, DE 100 18 918 A1 describe formulations containing polyether aziridines which show regular setting behavior.

25

For instance DE 100 58 846 A1 describes the use of N-alkyl aziridino polyethers containing methyl groups in the side chain to improve the properties of the uncured pastes at low temperatures. It is also described that 1 to 35 % by weight of solvents may be used related to the cured material. The solvents are chosen from the group of polyester polyols, aliphatic esters, oils, fats, aliphatic hydrocarbons, one- or

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multifunctional esters of multibasic acids, esters or amides of sulphonic acids.

58741EP002  
PE-8A/EP

DE 197 53 456 A1 mentions that solvents from 0 to 95 % by weight (related to the cured material) selected from polyetherpolyols, polyesterpolyols, polycarbonate polyols, aromatic hydrocarbons, aliphatic hydrocarbons, one- or multifunctional esters of multibasic acids, esters or amides of sulphonic acids may be used.

5 DE 100 18 918 A1 describes formulations of catalyst pastes. The catalyst pastes contain 0 to 95 % by weight of an inert solvent chosen from the group of polyether polyols, polyester polyols, aliphatic esters, oils, fats, waxes, aliphatic hydrocarbons, aliphatic hydrocarbons, one- or multifunctional esters of multibasic acids, esters or amides of sulphonic acids. The formulations comprise water (0,1 to 20 %) which is  
10 used to influence the speed of set and other properties of the catalyst paste and the cured rubber.

It is also described that the addition of water to a system of N-alkyl ethylene imines, solvent and initiators alters the speed of set and the conversion rate (G. D. Jones, D. C. MacWilliams, N. A. Braxton J. Org. Chem. 1965, 1994-2003). The addition of  
15 water to uncured polyether precision impression materials, however, may cause sticky surfaces when the impression is cured in the presence of additional water (or saliva in mouth) and may also negatively influence the precision of the impression when impregnated retraction cords or retraction solutions are used.

A further possibility to enhance the speed of set of formulations comprising  
20 compounds having aziridino groups is the additional use of monofunctional compounds together with multifunctional compounds.

In this respect the German patent application DE 10235990.3 describes a composition, wherein at least one compound has at least two ethylene imine groups and at least one compound has one ethylene imine group. However, the additional  
25 use of compounds having one ethylene imine group requires the increase of initiator. The increase of ethylene imine concentration and initiator results in high costs.

Impression materials based on polyvinyl siloxanes with short setting times are also known. Examples are 'Splash<sup>TM</sup> Half-Time (Discus), Aquasil<sup>TM</sup> Fast Set (Dentsply/Caulk), Imprint<sup>TM</sup> II Quick Step (3M ESPE AG), Take 1 Fast Set (Kerr),  
30 Extrude Extra (Kerr).

58741EP002  
PE-SA/EP

3

However, up to now there is no fast-setting polyether, especially no ethylene imine containing material available.

Considering the clinical situation, in most cases precision impression materials are used to obtain impressions of crowns, inlays, small implants or small bridges  
5 (approx. 80 %). In all these cases the dentist does not need a long total working time. In addition a short oral setting time also would be advantageous. Shortening both working time and oral setting time would save time for the dental professionals. Shortening of the whole rather uncomfortable impression taking would be advantageous to the patient.

10

It is thus an object of the present invention to alleviate one or more of the problems mentioned above.

It is also an object of the present invention to provide a composition with improved properties.

- 15 It is another object of the present invention to provide a composition, especially a dental polyether composition with enhanced speed of set without essentially altering the elastomeric properties of the cured material.

It has been found that one or more of the above mentioned objects can be achieved by providing a composition as described in the text below.

- 20 In this respect the present invention relates to a curable composition comprising

- an ethylene imine group containing component A,
- a SO<sub>2</sub>-NH group containing component B,
- an initiator C,
- optionally additives D like modifiers, fillers, dyes, pigments, thixotropic agents,  
25 flow improvers, polymeric thickeners, surfactants, odorous substances, diluting agent(s) and flavourings.

68741EP002

PE-SAVEP

Surprisingly it has been found that by adding a non-reactive accelerator the speed of set of the composition to be hardened can be accelerated without affecting the elastomeric properties of the vulcanized formulation to a considerable extent.

Adding a  $\text{SO}_2\text{-NH}$  group containing component to a curable ethylene imine group containing component enables one to provide compositions that are accelerated with respect to the speed of set without essentially varying the amount of reactive components. The  $\text{SO}_2\text{-NH}$  group containing compound usually does not alter the physical properties of the cured material to a considerable extent.

Using the present invention formulations can be provided fulfilling the requirements according to DIN EN ISO 4823:2000 of Type 0 (kneadable), Type 1 (high viscosity), Type 2 (medium viscosity), and Type 3 (low viscosity):

The present invention provides means to realize short(er) working times of curable compositions, especially dental impression materials, at room temperature and short oral setting times. A total working time at room temperature (23 °C) of less than 3:00 min according to DIN EN ISO 4823:2000 and an oral setting time of less than 3:30 min can be realized.

The total working time at room temperature (23 °C) can be measured according to DIN EN ISO 4823:2000. For instance, for Impregum<sup>TM</sup> Garant L DuoSoft and Permadyne Garant L 2:1 (3M ESPE AG), both Type 3 regular setting polyether precision impression materials, a working time of 3:40 min  $\pm$  0:15 min and 4:00  $\pm$  0:15 min, respectively, is measured.

The oral setting time is given by the manufacturer in the instructions for use. According to DIN EN ISO 4823:2000 the elastomeric property recovery from deformation of the vulcanized material have to reach values of  $\geq 96,5$  % within the recommended oral setting time. In addition according to DIN EN ISO 4823:2000 the elastomeric property strain in compression of the vulcanized material has to come up to a value within the range of 0,8 to 20,0 % for Type 0 and Type 1 materials and in the range of 2,0 to 20,0 % for Type 2 and Type 3 materials, respectively within the recommended oral setting time.

58741EP002  
PE-SA/EP

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For instance, for Permadyne™ Garant L 2:1 and Impregum™ Garant L DuoSoft (3M ESPE AG), both Type 3 regular setting polyether precision Impression materials an oral setting time of 3:30 min is advised by the manufacturer.

Often dental formulations are provided as two-compartment systems in which the  
5 two pastes are stored separately. The base paste contains the polymerizable compound(s) and is stored separately from the catalyst paste which contains the initiator.

With respect to shelf-life it is an advantage that the non-reactive accelerators used according to the present invention are compatible with the polymerizable  
10 compound(s) and with the initiator(s), as well.

An additional paste containing at least one accelerator might also be provided which can be used in dental offices to enhance the setting time of a given polyether Impression material according to the dentists needs.

The present invention provides therefore a low-cost and low-risk method to provide a  
15 quick-setting polyether Impression material.

The terms "comprise" and "contain" within the meaning of the invention introduce a non exhaustive list of features. Likewise, the word "one" or "a" is to be understood in the sense of "at least one".

20 "Working time" according to the present invention is the period between complete mixing of the components and the incipient curing of the mixed composition at room temperature. The end of the working time is regarded as the time at which a mixed composition displays pronounced changes such as skin formation or greatly reduced flowability. At the end of the working time the consistency of the mixed material does  
25 not allow the making of a precision impression with the desired detail reproduction and dimensional properties.

"Oral setting time" according to the present invention can be defined as the period between placing the dental tray in the mouth of the patient (the impression material is

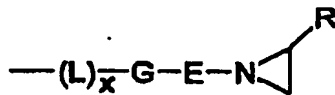
58741EP002  
PE-SA/EP

6

still processable) and the removal of the dental tray at the time the vulcanized impression material shows the desired elastomeric properties.

As ethylene imine group containing component A every component can be used which can be vulcanized in the presence of initiator C. The ethylene imine group containing component A comprises at least one ethylene imine group, preferably at least two ethylene imine group. Those components are known and described e.g. in US 3,453,242, DE 100 58 846 A1, DE 197 53 456 A1, DE 100 18 918 A1 and are generally known as N-alkyl aziridine polyether compositions.

Suitable components A are N-alkyl substituted aziridines attached to oligomeric and/or polymeric hydrocarbon, ester, ether or siloxane. The attached N-alkyl aziridine can be represented by the formula



wherein

R represents H, C<sub>1</sub>-C<sub>12</sub> alkyl, C<sub>2</sub>-C<sub>12</sub> alkenyl, C<sub>2</sub>-C<sub>12</sub> alkynyl, C<sub>7</sub>-C<sub>15</sub> alkylaryl, C<sub>7</sub>-C<sub>15</sub> arylalkyl, C<sub>3</sub>-C<sub>12</sub> cycloalkyl, and wherein hydrogen atoms may be replaced by Cl or F and/or wherein up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

E represents a C<sub>1</sub> - C<sub>18</sub> branched or unbranched hydrocarbon chain wherein up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

G represents a group selected from C(O)O, C(O)NR, C(O), C(O)C(O), C(O)(CH<sub>2</sub>)<sub>m</sub>C(O) with m = 1 to 10, C(S)NR, CH<sub>2</sub>,

L represents O, S, NR with x = 0 or 1.

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58741EP002  
PE-SAVEP

7

Component A is usually present in an amount in the range of 10 to 90 % by weight with respect to the cured composition.

For an impression material component A is preferably present in an amount in the range of 35 to 90 % by weight, more preferably in an amount in the range of 40 to 75 % by weight with respect to the cured composition.

For a of a duplicating material component A is preferably present in an amount in the range of 10 to 25 % by weight, more preferably in an amount in the range of 12 to 20 % by weight with respect to the cured composition.

The molecular weight ( $M_N$ ) of component A before setting is usually in the range of 600 to 20.000 g/mol, preferably in the range of 1.000 to 10.0000 g/mol, determined with GPC. Appropriate methods are known by the expert. In addition the determination of the molecular weight is possible using nuclear magnetic resonance spectroscopy (end-group determination). There are also applicable methods described in the literature for organic polyols that may be used like determination of hydroxyl number according to Houben-Weyl, "Methoden der organischen Chemie", 14/2, page 17, Georg Thieme Verlag, Stuttgart, 1963 or according to ASTM D2849 Method C.

A very useful method for determination of the molecular weight organic polyols is a GPC method using a combination of PSS SDV 10.000 Å + PSS SDV 500 Å with column dimensions 8x300 mm and a particle size of 5 µm. In addition a pre-column PSS SDV 100 Å with column dimensions 8x50 mm and a particle size of 10 µm is used. The eluent is THF stabilized with Jonol running with a flow rate of 1,0 ml/min. The detector is a refractive index detector (RI), the injection volume 100 µl. The samples have a concentration of 1 % (solvent THF). Polystyrol standards are used as the reference.

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As  $\text{SO}_2\text{-NH}$  group containing component B every component can be used, which is able to accelerate the speed of set of component A.

A sufficient acceleration of setting (measured at room temperature) of an impression material usually is achieved, if e.g. 4,0 % by weight of a non-reactive diluter of a

58741EP002  
PE-SAVEP

8

given formulation is replaced by the same amount of component B with the result that the Shore Hardness A (mean value determined from at least three samples) measured after 6 min according to DIN EN ISO 53505 increases by more than 30 %, preferably by more than 40 %, more preferably by more than 50 % with respect to

- 5 the value measured for the formulation without component B. Alternatively, e.g. 4.0 % by weight of component B may be added to a given formulation to attain the desired acceleration of set. For very soft rubbers like duplicating materials the acceleration in setting may be measured using a common oscillating rheometer monitoring  $G'$  and  $G''$ .

- 10 The  $\text{SO}_2\text{-NH}$  group containing component B comprises at least one  $\text{SO}_2\text{-NH}$  group, if needed at least two  $\text{SO}_2\text{-NH}$  groups. The  $\text{SO}_2\text{-NH}$  group containing component B can be a molecular or polymeric compound.

- Suitable components B are aryl sulfonic acid amides or alkyl sulfonic acid amides. In the sulfonamides one hydrogen atom attached to the nitrogen atom of the sulfonamide group may be replaced by an alkyl or aryl radical.

Component B can be represented e.g. by one of the following formulas:



wherein

- 20 R1 represents  $\text{C}_1\text{-C}_{22}$  alkyl,  $\text{C}_2\text{-C}_{22}$  alkenyl,  $\text{C}_2\text{-C}_{22}$  alkynyl,  $\text{C}_7\text{-C}_{22}$  arylalkyl or  $\text{C}_3\text{-C}_{22}$  cycloalkyl, and wherein one or more hydrogen atoms may be replaced by Cl or F and/or up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

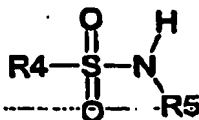
- R2 represents  $\text{C}_6\text{-C}_{18}$  aryl,  $\text{C}_7\text{-C}_{22}$  alkylaryl,  $\text{C}_2\text{-C}_{22}$  cycloalkylaryl,  $\text{C}_7\text{-C}_{22}$  alkenylaryl or  $\text{C}_7\text{-C}_{22}$  alkynylaryl, wherein one or more hydrogen atoms may be replaced by Cl or F and/or up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

R3 represents H, R1 or R2.

58741EP002  
PE-SAVEP

9

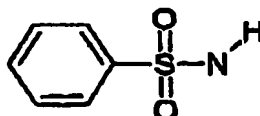
Also polymeric substances comprising the following structure may be used:



wherein R4 is R1 or R2,

and wherein R5 represents the chemical linkage to the polymer.

- 5 Component B contains preferably a sulfonic acid amide or mixture of sulfonic acid amides comprising an aromatic moiety, more preferably a structural element as described in the formula below



wherein the aromatic ring may be substituted by one or more substituents.

- 10 The sulfonic acid amide can be used alone or in admixture with other different sulfonic acid amides.

Particularly preferred are benzene sulfonic acid N-butyl amide, p-toluene sulfonic acid N-ethyl amide or a mixture of o-/p-toluene sulfonic acid N-ethyl amide.

- Component B is usually present in an amount in the range of 0,01 to 20,0, preferably  
15 in the range of 0,1 to 10,0, more preferably in the range of 0,2 to 6,0 % by weight with respect to the cured composition.

The molecular weight of component B is usually in the range of 90 to 2000 g mol<sup>-1</sup> preferably in the range of 90 to 300 g mol<sup>-1</sup>.

- 20 As initiator C every component can be used, which is able to start the curing process of component A.

58741EP002

PE-SA/EP

The molar ratio between the initiator and the N-alkyl substituted aziridines of the formulation usually is in the range of  $\text{gmol}^{-1}$  from 1,0:0,1 to 1,0:20,0, preferably in the range of 1,0:0,5 to 1,0:10,0, more preferably in the range from 1,0:0,8 to 1,0:3,0.

~~Suitable initiators can be found in O.C. Dermer, G. E. Ham "Ethylenimine and other~~  
5 **Aziridines " Academic Press (1969).**

Particularly useful are the substituted alkyl sulfonium salts described in US 4,167,618 incorporated herein by reference.

Optionally additives like modifiers, fillers, dyes, pigments, thixotropic agents, flow improvers, polymeric thickeners, surfactants, odorous substances, diluters and  
10 flavourings can be added. Additional substances might be useful to further adjust the rheological characteristics.

The additive(s) is(are) usually present in an amount in the range of 10 to 90 % by weight with respect to the cured composition. For impression materials the additive(s) is preferably present in an amount in the range of 10 to 65 %, more  
15 preferably in the range of 25 to 60 % with respect to the cured composition. For duplicating materials the additive(s) is preferably present in the range of 10 to 90 %, more preferably in the range of 20 to 85 % by weight with respect to the cured composition.

Suitable filler(s) are aluminosilicates, silicic acids, quartz powder, wollastonite, mica  
20 powder and diatomaceous earth.

Suitable thixotropic agent(s) are surface treated silica and/or waxes according to the definition in Ullmanns Enzyklopädie der technischen Chemie, 4. Auflage, Verlag Chemie, Weinheim, Band 24, page 3. Especially useful are triglycerides as described in DE 197 11 514 A1.

25 Suitable surfactant(s) are polyethers and polyether type materials with special structures such as Pluronic<sup>TM</sup>, Synperonic<sup>TM</sup>, Silwet<sup>TM</sup> type materials. Especially useful are substances described in DE 43 06 997 A1.

Suitable diluting agent(s) are liquids such as C<sub>12</sub>-C<sub>15</sub> alkyl acetates, liquid derivatives of citric acid, esters of phthalic acid with branched alcohols like bis(2-

58741EP002  
PE-SA/EP

11

ethylhexyl)phthalate or polymeric phthalates,  $C_2-C_{18}$  bis(alkyl)esters of  $C_2-C_8$  dicarboxylic acids like dioctylmaleate, aromatic and aliphatic esters of sulfonic acids like Mesamoll<sup>TM</sup>, derivatives of di- and tri-ethylen and -propylene glycol, typical aromatic diluters like poly-phenyls, dibenzyl-toluene, xylyl-toluene, dixylyl-toluene and

5 polymeric compounds like polyethers, polyesters, polycarbonates, polyolefines. From the group of polymeric compounds, compounds with hydroxyl, ether, alkyl, ester functions are preferred.

10 The shore hardness A of the compositions of the present invention is measured according to DIN 53505. To monitor the speed of set time-dependent measurements were performed.

The shore hardness A measured after 24 hours usually is in the range from 40 to 80 for impression materials and in the range from 10 to 40 for duplicating materials.

15 The elongation at break according to DIN 50125 of the cured impression material of the present invention measured 24 hours after mixing the components usually is  $\geq 40$  %, preferably  $\geq 50$  % more preferably  $\geq 60$  %.

The tensile strength according to DIN 50125 of the cured impression material of the present invention measured 24 hours after mixing the components usually is  $\geq 0,50$  MPa, preferably  $\geq 0,55$  MPa more preferably  $\geq 0,60$  MPa.

20 The elongation at break according to DIN 50125 of the cured duplicating material of the present invention measured 24 hours after mixing the components usually is  $\geq 80$  %, preferably  $\geq 100$  % more preferably  $\geq 120$  %.

The tensile strength according to DIN 50125 of the cured duplicating material of the present invention measured 24 hours after mixing the components usually is  $\geq 0,20$  MPa, preferably  $\geq 0,25$  MPa more preferably  $\geq 0,30$  MPa.

25 As mentioned above dental formulations are often provided as two-component systems.

58741EP002  
PE-SA/EP

12

Therefore, the present invention also relates to a kit of parts, wherein the base part comprises component A, the catalyst part comprises component C, and wherein component B is present either in the base part or the catalyst part or in the base part and the catalyst part.

- 5 However, the accelerating effect of component B can also be used to enhance the speed of set of component A containing compositions described in the state of the art.

Presently, the following components are available on the market: Materials of Type 1, (comparable to Permadyne™ Penta™ H, Permadyne™ fest, Impregum™ Penta™ H  
10 DuoSoft™), Type 2 (comparable to Impregum™ F, Impregum™ Penta™, Impregum™ Penta™ Soft) and Type 3 (comparable to Permadyne™ Penta™ L, Permadyne™ Garant™ 2 : 1, Permadyne™ dünn, Impregum™ Penta™ L DuoSoft™, Impregum™ Garant™ L DuoSoft™). All materials are available from 3M ESPE AG.

Therefore, the present invention relates also to a kit of parts, wherein component B  
15 is comprised in a further part and neither comprised in the catalyst part nor in the base part.

The present invention also relates to a method of producing a curable composition comprising the steps a) providing components A, B and C, b) mixing the components.

- 20 The dosing of the components can be carried out by sight (strand-length comparison), by weight, via pre-dosed pack units and subsequent manual mixing, from double-chambered cartridges with static mixing tubes or by means of volume dosing systems with downstream static or dynamic mixers.

A mixing device can be used as it is described in EP 0 492 413 B1 and available on  
25 the market as Pentamix™ or Pentamix™ 2. Mixing, however, can also be achieved manually.

A further subject of the invention are packages containing components of the composition, in particular cartridges, bags, prefilled dental trays.

58741EP002  
PE-SA/EP

13

The composition according to the invention can advantageously be used for modeling of objects or body parts. The composition of the present invention is particularly useful as a dental impression material, especially as a precision impression material, as a bite registration material or duplicating material.

5 The composition of the present invention does not necessarily comprise water.

In addition the composition does not necessarily comprise sulfonamides used as active agents in drugs or herbicides.

The present invention is hereinafter described by examples.

10

#### Measurements

Measuring Shore Hardness A is a very convenient method to obtain data about the degree of vulcanization. The value of Shore Hardness is a common number in dentistry to characterize the vulcanized impression. Time dependant measurements were done according to DIN 53505. For determination of the values three independent measurements were performed. A "Handhärteprüfgerät Zwick 3150" (Zwick GmbH & Co, Ulm) was used as the measuring device. The accuracy of the given values is  $\pm 1$ .

15

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Tensile strength and elongation at break were measured according to DIN 50125 Form B. The sample was  $6.0 \pm 0.1$  mm in diameter and  $50.0 \pm 0.1$  mm in lengths (Zugprobe B 6 x 50 DIN 50125). For determination of the values five independent measurements were performed. A "Universalprüfmaschine Zwick 1435" (Zwick GmbH & Co, Ulm) was used as the measuring device.

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#### Formulations:

##### Base Paste 1

30

81,0 % difunctional aziridino polyether (EO (ethylene oxide) / THF (tetra hydro furan) polyether back bone; Mn: 6000)

68741EP002  
PE-SA/EP

14

7,0 % fat (triscacylic ester of glycerine)  
1,0 % surfactant (copolymer EO/PO)  
9,5 % dibenzyl toluene  
1,5 % diatomaceous earth

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**Base Paste 2**

81,0 % difunctional aziridino polyether (Mn: 6000)  
7,0 % fat (triscacylic ester of glycerine)  
1,0 % surfactant (copolymer of EO/PO)  
10 8,8 % dibenzyl toluene  
1,5 % diatomaceous earth  
0,7 % imidazole compound

**Catalyst Paste 1**

15 14,0 % sulfonium salt tetrafluoroborate  
20,0 % acetyl tributyl citrate  
29,0 % unreactive polyether (Mn: 6000)  
12,0 % dibenzyl toluene  
3,0 % surfactant (copolymer EO/PO)  
20 11,0 % diatomaceous earth  
11,0 % highly dispersed silica, surface treated

**Catalyst Paste 2**

13,5 % sulfonium salt tetrafluoroborate  
25 19,0 % acetyl tributyl citrate  
29,0 % unreactive polyether (Mn: 6000)  
6,5 % dibenzyl toluene  
3,0 % surfactant (copolymer EO/PO)  
24,0 % diatomaceous earth  
30 5,0 % highly dispersed silica, surface treated



58741EP002  
PE-SA/EP

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### I. Varying the amount of sulfonamide

A)

2,0 g of Base-Paste 1 was mixed together with 1.2 g of Catalyst Paste 2. Entry 1, DI-.....

- 5 benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of bezene sulfonic acid N-butyl amide (CAS-No 3622-84-2). Entry 2-5.

Table 1

Entry	Amount of benzene sulfonic acid N- butyl amide in the		Shore-Hardness A after					
	Elastomer	Base Paste	6 min	8 min	10 min	15 min	30 min	24 h
1	0,00 %	0,00 %	27	37	42	49	52	53
2	1,25 %	2,00 %	38	45	48	51	53	53
3	2,50 %	4,00 %	41	47	50	53	54	54
4	3,75 %	6,00 %	46	49	51	53	54	54
5	5,00 %	8,00 %	47	50	51	53	54	54

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Table 2

Entry	Amount of benzene sulfonic acid N- butyl amide			
	Elastomer	Base Paste	Tensile Strength	Elongation at break
1	0,00 %	0,00 %	1,04 ± 0,03 MPa	78 ± 6 %
3	2,50 %	4,00 %	0,99 ± 0,05 MPa	75 ± 8 %
5	5,00 %	8,00 %	1,12 ± 0,15 MPa	91 ± 23 %

58741EP002

PE-SA/EP

16

B)

The 2,0 g of altered Base Paste 1 that already contains 8,00 % of benzene sulfonic acid N-butyl amide (CAS-No 3622-84-2) was used together with 1,2 g of Catalyst

5 Paste 2, Entry 5.

Acetyl tributyl citrate (CAS-No 77-90-7) in the Catalyst Paste 2 was replaced by the same amount of benzene sulfonic acid N-butyl amide (CAS-No 3622-84-2). 2,0 g of the base paste according to Entry 5 was used with 1,2 g of the altered catalyst pastes, Entry 6.- 7.

10

Table 3

Entry	Amount of benzene sulfonic acid N-butyl amide in the			Shore-Hardness A after					
	Elastomer	Base Paste	Catalyst Paste	6 min	8 min	10 min	15 min	30 min	24 h
5	5,00 %	8,00 %	0,00 %	47	50	51	53	54	54
6	6,25 %	8,00 %	3,33 %	47	50	52	53	53	53
7	7,50 %	8,00 %	6,67 %	48	51	53	53	53	53

15

From the above it becomes clear that the addition of component B does not have a significant effect on the elastomeric properties of the cured composition. Tensile strength and elongation at break remain essentially unchanged.

However, as can be inferred especially from Table 1 a sufficient Shore Hardness A can be achieved after a shorter period of time, if component B is present in the composition.

58741EP002

PE-SAVEP

17

It also becomes clear, that the desired effect can be already achieved at a considerable low concentration of the sulfonamide component and that further increasing the concentration does not necessarily enhance the speed of set.

### 5 II. Comparison: Sulfonamide used in the catalyst paste vs. sulfonamide used in the base paste

Base Paste 2 and Catalyst Paste 1 were altered. 2,0 g of the used base paste was mixed together with 1,1 g catalyst.

10 Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of bezene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 8.

Acetyl tributyl citrate (CAS-No 77-90-7) in the catalyst paste was replaced by the same amount of bezene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 9.

Table 4

15

Entry	Amount of benzene sulfonic acid N-butyl amide in the			Shore-Hardness A after					
	Elastomer	Base Paste	Catalyst Paste	6 min	8 min	10 min	15 min	30 min	24 h
8	2,26 %	3,50 %	0,00 %	28	36	40	45	46	47
9	2,26 %	0,00 %	6,40 %	29	36	40	43	48	49

The results show that there is no significant difference whether the sulfonamide is used in the base paste or in the catalyst paste.

20

### III. Comparison: Use of mixture of o-/p- toluene sulfonic acid N-ethyl amide vs. use of bezene sulfonic acid N-butyl amide and p- toluene sulfonic acid N-ethyl amide

2,0 g Base Paste 2. was mixed together with 1,2 g of Catalyst Paste 2, Entry 10.

68741EP002  
PE-SAVEP

18

Base Paste 2 was altered. 2,0 g of altered Base Paste 2 was mixed together with 1,2 g of Catalyst Paste 2.

5 Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of mixture approx. 70 : 30 mixture of o-/p- toluene sulfonic acid N-ethyl amide (CAS-No 8047-99-2, 26914-52-3), Entry 11.

Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of benzene sulfonic acid N-butyl amide (CAS-No 80-39-7), Entry 12.

10 Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of benzene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 13.

Table 5

Entry	Used sulphonamide	Amount of Sulfonamide in the		Shore-Hardness A after					
		Elasto-mer	Base Paste	6 min	8 min	10 min	15 min	30 min	24 h
10	None	0,00 %	0,00 %	18	28	34	42	48	50
11	o-/p-toluene sulfonic acid N-ethyl amide	3,75 %	6,00 %	31	38	41	46	49	50
12	p-toluene sulfonic acid N-ethyl amide	3,75 %	6,00 %	34	40	42	47	50	51
13	benzene sulfonic acid N-butyl amide	3,75 %	6,00 %	30	37	42	46	50	50

15 The results show that various sulfonamides with alkyl substituents at the SO<sub>2</sub>-NH-group can be used to achieve the desired acceleration in the speed of set.

58741EP002  
PE-SA/EP

19

**IV. Comparison: Use of bezene sulfonic acid N-butyl amide vs. benzene sulfonic acide amide****Base Paste 2 was altered. 2.0 g of altered Base Paste 2 was mixed together with 1.2****5 g of Catalyst Paste 2.****Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of bezene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 13.****Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of benzene sulfonic acid amide (CAS-No 98-10-2), Entry 14.**

10

**Table 6**

Entry	Used sulphonamide	Amount of Sulfonamide in		Shore-Hardness A after					
		Elasto- mer	Base Paste	6 min	8 min	10 min	15 min	30 min	24 h
13	benzene sulfonic acid N-butyl amide	3,75 %	6,00 %	30	37	42	46	50	50
14	benzene sulfonic acid amide	3,75 %	6,00 %	33	40	42	47	49	49

**The results show that sulfonamides with alkyl substituents at the SO<sub>2</sub>-NH-group and**

**15 sulfonamides with SO<sub>2</sub>-NH<sub>2</sub> groups can be used, as well, to achieve the desired acceleration in the speed of set.**

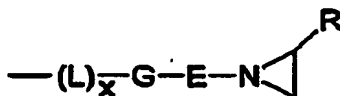
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58741EP002  
PE-SAVEP

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**Claims:****1. Composition comprising with respect to the cured composition**

- 5 -----an-ethylene-imine-group-containing-component-A,-----  
 a SO<sub>2</sub>-NH group containing component B,  
 an Initiator C,  
 optionally additives D comprising modifiers, fillers, dyes, pigments, thixotropic  
 agents, flow improvers, polymeric thickeners, surfactants, odorous  
 10 substances, diluting agent(s) and flavourings.

**2. The composition according to claim 1, wherein component A comprises a structure element represented by the following formula**

15 wherein

R represents H, C<sub>1</sub>-C<sub>12</sub> alkyl, C<sub>2</sub>-C<sub>12</sub> alkenyl, C<sub>2</sub>-C<sub>12</sub> alkynyl, C<sub>7</sub>-C<sub>15</sub> alkylaryl, C<sub>7</sub>-C<sub>15</sub> arylalkyl, C<sub>3</sub>-C<sub>12</sub> cycloalkyl, and wherein hydrogen atoms may be replaced by Cl or F and/or wherein up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

20 E represents a C<sub>1</sub> - C<sub>18</sub> branched or unbranched hydrocarbon chain wherein up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

G represents a group selected from C(O)O, C(O)NR, C(O), C(O)C(O), C(O)(CH<sub>2</sub>)<sub>m</sub>C(O) with m = 1 to 10, C(S)NR, CH<sub>2</sub>,

25 L represents O, S, NR with x = 0 or 1.

**3. The composition according to anyone of the preceding claims comprising component B in an amount of 0,01 % by weight to 20,00 % by weight.**

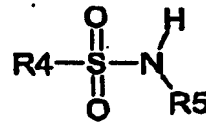
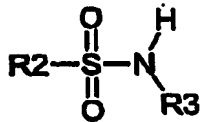
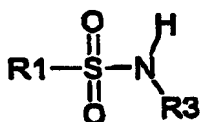
58741EP002  
PE-SAVEP

21

4. The composition according to anyone of the preceding claims, wherein component B comprises aryl sulfonic acid amides and/or alkyl sulfonic acid amides.

5 5. The composition according to anyone of the preceding claims, wherein component B comprises N-alkyl or N-aryl substituted aryl sulfonic acid amides and/or N-alkyl or N-aryl substituted alkyl sulfonic acid amides.

10 6. The composition according to anyone of the preceding claims, wherein component B is represented by at least one of the following formulas:



wherein

15 R1 represents C<sub>1</sub>-C<sub>22</sub> alkyl, C<sub>2</sub>-C<sub>22</sub> alkenyl, C<sub>2</sub>-C<sub>22</sub> alkynyl, C<sub>7</sub>-C<sub>22</sub> arylalkyl or C<sub>3</sub>-C<sub>22</sub> cycloalkyl, and wherein one or more hydrogen atoms may be replaced by Cl or F and/or up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

20 R2 represents C<sub>6</sub>-C<sub>18</sub> aryl, C<sub>7</sub>-C<sub>22</sub> alkylaryl, C<sub>2</sub>-C<sub>22</sub> cycloalkylaryl, C<sub>7</sub>-C<sub>22</sub> alkenylaryl or C<sub>7</sub>-C<sub>22</sub> alkynylaryl, wherein one or more hydrogen atoms may be replaced by Cl or F and/or up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

R3 represents H, R1 or R2.

R4 is R1 or R2,

25 and R5 represents the chemical linkage to a polymer.

68741EP002

PE-SA/EP

7. The composition according to anyone of the preceding claims, wherein the molecular weight of component B is in the range of 90 to 2000 g/mol<sup>1</sup>.

~~8. The composition according to anyone of the preceding claims, wherein~~

5 component B comprises benzene sulfonic acid N-butyl amide or p-toluene sulfonic acid N-ethyl amide, o-toluene sulfonic acid N-ethyl amide, benzene sulfonic acid amide or a mixture of o-/p- toluene sulfonic acid N-ethyl amide.

10 9. The composition according to anyone of the preceding claims, wherein initiator C is selected from the group of protonating or alkylating agents or wherein the initiator C generates protons and/or reactive alkylating agents in a chemical reaction.

15 10. The composition according to anyone of the preceding claims having a working time at 23 °C of equal or less than 3:30 min according to DIN EN ISO 4823:2000 and/or an oral setting time of equal or less than 3:30 min

20 11. Kit of parts, comprising a base and a catalyst part, wherein the base part comprises component A, the catalyst part comprises component C, and wherein component B is present either in the base part or the catalyst part or in the base part and the catalyst part, wherein components A, B and C have the meaning as defined in the preceding claims.

25 12. Kit of parts, wherein the base part comprises component A, the catalyst part comprises component C, and wherein component B is comprised in a further part and neither comprised in the catalyst part nor in the base part, wherein components A, B and C have the meaning as defined in the preceding claims.

30 13. Method of producing a composition according to one of the claims 1 to 10 comprising the steps a) providing components A, B and C, b) mixing the components.



58741EP002  
PE-SAVEP

23

14. Use of a component B containing composition for enhancing the speed of set of a component A and C containing composition, wherein components A, B and C have the meaning as defined in the preceding claims.

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15. Use of the composition according to anyone of claims 1 to 9 or the kit of parts according to claim 10 or 11 for modeling of objects or body parts, preferably as dental impression, bite registration or dental duplicating material.

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58741EP002  
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24

### Abstract

5 The present invention relates to a composition with enhanced speed of set, especially to a method of making rubber-like elastomers with improved hardening characteristics. In this respect the present invention provides a composition comprising with respect to the cured composition a ethylene imine group containing component A, a  $\text{SO}_2\text{-NH}$  group containing component B and an initiator C. Optionally  
10 additives like modifiers, fillers, dyes, pigments, thixotropic agents, flow improvers, polymeric thickeners, surfactants, odorous substances, diluters and flavourings can be added

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